

Sertifikaat

REPUBLIEK VAN SUID-AFRIKA

PATENT KANTOOR
DEPARTEMENT VAN HANDEL
EN NYWERHEID



Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE
DEPARTMENT OF TRADE AND
INDUSTRY

Hiermee word gesertifiseer dat
This is to certify that

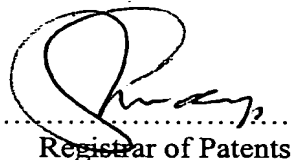
the documents annexed hereto are true copies of:

Application forms P.1 and P.2, provisional specification and drawings
of South African Patent Application No. 2001/4793 as originally filed
in the Republic of South Africa on 13 June 2001 in the name of
BILLITON SA LIMITED for an invention entitled: " EXTRACTION MIXTURE
FOR THE PURIFICATION OF BASE METALS ".

Geteken te
Signed at
PRETORIA

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

30th dag van
day of
June 2004


Registrar of Patents

REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

REGISTRAR OF PATENTS

Official Application No.			Lodging date: Provisional			Acceptance date:		
21	01	20014793	22	13 JUNE 2001	47			
International classification			Lodging date: Complete			Granted date:		
51			23					
Full name(s) of applicant(s)/Patentee(s)								
71	BILLITON SA LIMITED							
Applicant(s) substituted:						Date Registered:		
71								
Assignee(s):						Date Registered:		
71								
Full name(s) of inventor(s)								
72	SCHAEKERS, Jozef, Marie and DU PREEZ, Jan Gysbert, Hermanus							
Priority claimed		Country		Number		Date		
Note: Use International Abbreviation for Country	33	NONE	31	NONE	32	NONE		
	33		31		32			
	33		31		32			
Title of Invention:								
54	EXTRACTION MIXTURE FOR THE PURIFICATION OF BASE METALS							
Address of applicant(s)/patentee(s)								
200 Hans Strijdom Drive, Randburg, 2125								
Address for Service:								
74	McCALLUM, RADEMEYER & FREIMOND, Maclyn House, June Avenue, Bordeaux, Randburg • P.O. Box 1130, Randburg 2125							
Patent of Addition No.			Date of any change:					
61								
Fresh Application based on:			Date of any change:					

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

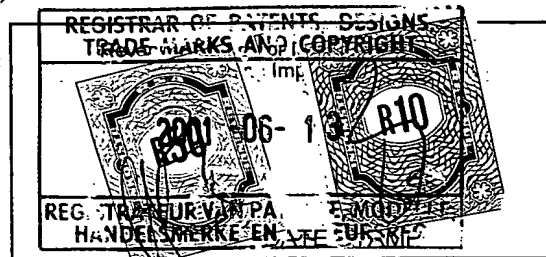
APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF
RECEIPT

(Section 30(1) - Regulation 22)

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

21	01	20014793
----	----	----------



FULL NAME(S) OF APPLICANT(S)

71	BILLITON SA LIMITED
----	---------------------

ADDRESS(ES) OF APPLICANT(S)

200 Hans Strijdom Drive, Randburg, 2125

TITLE OF INVENTION

54	EXTRACTION MIXTURE FOR THE PURIFICATION OF BASE METALS
----	--

Priority is claimed as set out on the accompanying Form P2.

The earliest priority claimed is :

This application is a patent of addition to Patent Application No.	21	01	
--	----	----	--

This application is a fresh application in terms of section 37 and based on Application No.	21	01	
---	----	----	--

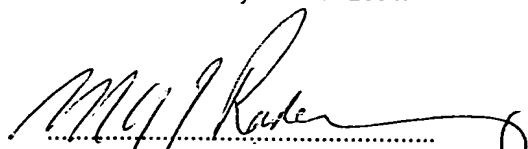
THIS APPLICATION IS ACCOMPANIED BY:

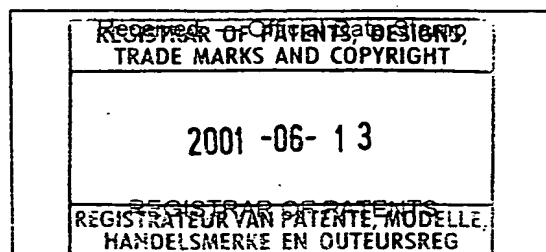
<input checked="" type="checkbox"/>	1	A single copy of a provisional specification of 19 pages
<input type="checkbox"/>	2	Two copies of a complete specification of pages
<input checked="" type="checkbox"/>	3	6 sheets of Informal Drawings
<input type="checkbox"/>	4 sheets of Formal Drawings
<input type="checkbox"/>	5	Publication particulars and abstract (Form P8 in duplicate)
<input type="checkbox"/>	6	A copy of Figure of drawings (if any) for the abstract
<input type="checkbox"/>	7	Assignment of Invention
<input type="checkbox"/>	8	Certified priority document(s) Number(s)
<input type="checkbox"/>	9	Translation of priority document(s)
<input type="checkbox"/>	10	An assignment of priority rights
<input type="checkbox"/>	11	A copy of the Form P2 and the specification of SA Patent Application No.
<input type="checkbox"/>	12	A declaration and power of attorney on Form P3
<input type="checkbox"/>	13	Request for ante-dating on Form P4
<input type="checkbox"/>	14	Request for classification on Form P9
<input checked="" type="checkbox"/>	15	Form P2 in duplicate

21	01	
----	----	--

74	ADDRESS FOR SERVICE: McCALLUM, RADEMEYER & FREIMOND, Maclyn House, June Avenue, Bordeaux P.O. Box 1130, Randburg, 2125
----	--

Dated this 13th day of June 2001.


McCALLUM, RADEMEYER & FREIMOND
PATENT AGENTS FOR APPLICANT(S)



REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

PROVISIONAL SPECIFICATION

(Section 30(1) - Regulation 27)

OFFICIAL APPLICATION NO

21	01	20014793
----	----	-----------------

LODGING DATE

22	13 JUNE 2001
----	--------------

FULL NAME(S) OF APPLICANT(S)

71	BILLITON SA LIMITED
----	---------------------

FULL NAME(S) OF INVENTOR(S)

72	SCHAEKERS, Jozef, Marie and DU PREEZ, Jan Gysbert, Hermanus
----	---

TITLE OF INVENTION

54	EXTRACTION MIXTURE FOR THE PURIFICATION OF BASE METALS
----	--

BACKGROUND OF THE INVENTION

This invention relates to a mixture of organic compounds suitable for the solvent extraction-based separation and purification of base metals and associated impurities from weakly acidic sulphate solutions.

5 Hydrometallurgical methods to recover base metals from ores, concentrates or intermediates have increased in popularity due to the perceived reduced environmental impact in comparison with smelting operations. Their application is frequently hindered by the lack of
10 suitable methods for the selective recovery of the metals of interest in a pure form.

Acidic sulphate solutions could be obtained by direct acid leaching of processing residues, ores or concentrates containing oxides and/or secondary sulphides of base metals. They could also be obtained by
15 treating similar but more refractory materials by low pressure oxidation (Activox process), standard pressure oxidation or bioleaching of sulphides, or high temperature acid leaching of refractory oxide ores.

The resulting aqueous sulphate solution, which could also contain other anions such as chloride and nitrate, mostly contains the base metals Cu, Ni, Co, Zn, Cd and Pb, additional impurities such as Mn, Fe(II), Fe(III),
20 and the alkaline earth metals Ca and Mg, their relative concentrations depending on the ore/intermediate being treated.

The removal of appreciable amounts of copper from such solutions can be effected by selective cementation with scrap iron or by solvent extraction (SX) with hydroxy-oxime based extractants (LIX-
25 extractants).^(1,2) In both instances, the presence of ferric ions in the leach solution will affect the efficiency of the downstream recovery process and its efficient removal is highly recommended but not always readily achieved, not even with hydroxy-oxime based extractants.

Pregnant solutions obtained by leaching zinc oxide ores or roasted sulphide concentrates or direct bioleaching of sulphides, are traditionally treated by a combination of neutralisation/precipitation and cementation to remove undesirable impurities such as Fe, Ni, Co, Cu, Cd and Pb before electrowinning (EW).⁽³⁻⁷⁾ This is normally associated with appreciable losses of zinc. More recently, SX has also been used as a means of purifying the primary leach liquor with the added advantage that the zinc content of the pregnant liquor can be increased to suit subsequent EW requirements.

The preferred extractant appears to be di-2-ethyl hexyl phosphoric acid (DEHPA) which is not very selective for zinc and tends to co-extract impurities such as Fe, Al, Pb, Cd and Ca if a raffinate with a low zinc content is required.^(8,9)

Treatment of nickel/cobalt pregnant solutions tends to be more complicated. The main impurities in such solutions are typically Fe, Mn, Ca, Mg, Cu and, to a lesser extent, Zn. The separation of nickel and cobalt can readily be effected with a SX reagent such as bis (2,4,4-triethylpentyl)-phosphinic acid (CYANEX 272), but this does not offer the opportunity of removing impurities as required for the subsequent EW process.⁽¹⁰⁻¹³⁾

Various strategies have been developed to effect the purification and separation required to obtain high purity products in the form of salts, oxides or metals.

In the more traditional downstream treatment procedure, the weakly acidic sulphate solution is treated with sulphide to selectively precipitate the base metals and effect removal of other dissolved impurities, mainly Mn, Ca, Mg and other alkaline earth or alkali metals.⁽¹³⁻¹⁵⁾ The main disadvantage of this option is that the precipitate needs to be redissolved

by pressure oxidation before further purification and separation of cobalt and nickel can be considered.

In an alternative option, the base metals are precipitated as hydroxides by neutralising the solution with MgO or CaO.⁽¹⁶⁻²¹⁾ The main advantage of this procedure is that the base metals in the precipitate can be re-leached in ammonia, ammonium sulphate or ammonium carbonate solutions at atmospheric pressure. The main disadvantage, in comparison with sulphide precipitation, is that rejection of manganese and the alkaline earth metals is less efficient as they tend to coprecipitate with the base metals. They are, however, largely insoluble during re-leaching but the presence of manganese tends to cause incomplete recovery of nickel and cobalt necessitating an additional strong acid leaching stage to prevent losses of these metals.

Further potential solutions are based on SX only, eventually after removal of Fe, Al and Cr by neutralisation/precipitation.

In one proposed option, base metals are selectively extracted from strongly acidic solutions with a di-thiophosphinic acid commercial extractant (CYANEX 301) leaving Ca, Mg and Mn in the raffinate. Subsequently, the base metals are stripped from the organic phase for further separation and purification.⁽²²⁾

Other systems, under investigation or proposed, usually involve the use of a carboxylic acid (typically Versatic acid), a di-alkyl phosphoric acid (DEHPA) and CYANEX 272 in various configurations.^(10-12,21) In these instances, Versatic acid is mainly used to remove the majority of Mn, Ca and Mg without major losses of base metals, but does not offer any possibility of separating any of the base metals. It also has the disadvantage of high water solubility at the elevated pH required for effective nickel/cobalt recovery.

Better rejection of undesired impurities, and especially calcium and manganese, can be achieved by adding a synergistic compound to the Versatic acid extraction mixture with an associated reduced pH for effective extraction as an added advantage.⁽²³⁻²⁶⁾ As

an alternative extraction can be done on the acidic solution, obtained by the Versatic acid mixture, with a DEHPA based extraction mixture to remove further amounts of calcium and manganese. The advantage of also removing Zn, Pb, Cd and Cu if present, may justify the use of SX to remove trace amounts of impurities which is very cost effective. In addition, extreme care must be taken to prevent loss of nickel/cobalt during this step.

CYANEX 272 is frequently used to separate cobalt and nickel, either before or after removing Ca, Mg and Mn impurities using Versatic acid mixture. Other base metals, if still present, are co-extracted and separation techniques, such as selective stripping, are required to obtain a highly free solution suitable to produce a high purity product.

From the above discussions it is clear that an extraction mixture capable of removing the impurities to obtain purified base metal sulphate solution, to be converted to high purity products, will be of great benefit to the industry as it will reduce the complexity of the processes and associated costs.

OBJECT COMPOSITION

It is an object of the present invention to provide a mixture of organic compounds which is suitable to be used as a solvent extractant mixture to treat acidic sulphate solutions which is capable of:

- a) selectively extracting impurities including manganese, lead, alkaline earth metals and ammonium ions;

- b) selectively extracting groups of certain base metals by direct extraction or by differential stripping or by a combination of these; and
 c) selectively removing single base metals by direct extraction or by differential stripping.

5 SUMMARY OF THE INVENTION

This invention provides an organic solvent extraction mixture which includes:

- a) an extractant, which is a substituted imidazole (Diagram 1) or benzimidazole (Diagram 2)

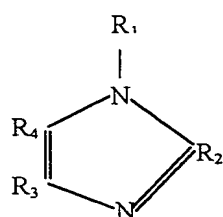


Diagram 1

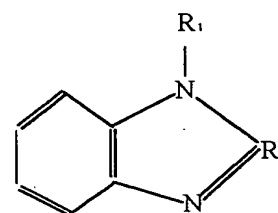


Diagram 2

and wherein the substituents are:

- R_1 = an organic group which :

- is branched or unbranched;
- is saturated or partly unsaturated;
- contains aromatic groups or not;
- is with or without other functional groups; or
- is an esterified fatty acid group;

and wherein R_1 may have between 2 and 20 carbon atoms and preferably has between 6 and 15 carbon atoms;

- R_3 = a hydrogen atom or a short chain organic group with between 1 and 2 carbon atoms, preferably hydrogen or a methyl group;

- R₄ = a hydrogen atom or a short chain organic group with between 1 and 2 carbon atoms, preferably hydrogen or a methyl group;
- R₂ = a -2-pyridine group in which the pyridine group can be substituted or unsubstituted; or
- = a -methylene-1-pyrazole group in which the pyrazole group can be substituted or unsubstituted; or
- = an imidazole based group, which may be a mirror image of the compounds shown in Diagrams 1 and 2; or
- = a methylene-amino group as shown in Diagram 3

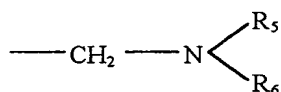


Diagram 3

and wherein

- R₅ = a hydrogen or a methyl group;
- R₆ = a hydrogen or an aliphatic group, branched or unbranched, containing between one and 10 carbon atoms; or
- = a methylene-amino group (see Diagram 3) with one of the substituents either being a hydrogen or a methyl group and the other a hydrogen or an aliphatic group, branched or unbranched, containing between one and 10 carbon atoms; or
- = a -2-pyridine group in which the pyridine group can be substituted or unsubstituted; or
- = a -methylene-1-pyrazole group in which the pyrazole group can be substituted or unsubstituted; or

= a 2-methyl imidazole based group which may be a mirror image of the compound shown in Diagram 1 or Diagram 2.

5 The concentration of the extractant can be between 0.01 and 1.50 Molar, depending on the capacity required and preferably lies between 0.25 and 1.50 Molar for commercial applications;

10 b) a non selective strongly acidic cation extractant, such as a sulphonic acid ($R-SO_3H$), to facilitate phase transfer of base metal ions from an aqueous weakly acidic sulphate solution into the organic phase, and wherein R is an aliphatic group, either saturated or unsaturated and branched or unbranched, an aromatic organic group or a mixed group consisting of both aliphatic and aromatic parts, with between 3 and 40 carbon atoms, preferably with between 8 and 30 carbon atoms.

15 Typical examples include: di-nonyl naphthalene sulphonic acid (DNNS), di-dodecyl naphthalene sulphonic acid, di-n-octyl methyl sulphonic acid and alkyl substituted benzene sulphonic acids which are commercially available or easy to synthesise.

20 The concentration of this compound may be between 0.001 to 1.0 Molar sulphonic acid, preferably between 0.10 to 0.50 Molar, the optimum being 20% to 25% of the extractant concentration and 50% to 100% of the maximum metal molarity in the organic phase;

25 c) a modifier to improve the characteristics of the organic phase with respect to metal complex solubility to avoid third phase formation, completeness and ease of stripping, viscosity and phase disengagement. Said modifier being characterized by the presence of a sterically available oxygen or nitrogen atom with lone pairs of electrons as in phenols, alcohols, esters of inorganic and organic acids, ketones, aldehydes, ethers, organic acids, amines and amides.

Eventually, a mixture of some of the above compounds could be used to obtain the desired effect.

The modifier may be added at a concentration of 10% to 70% and preferably at a concentration of 20% to 40% of the total mixture; and

- 5 d) a diluent, which is selected from a non-specific aliphatic or aromatic or partly aliphatic, partly aromatic mixture of unspecified composition with a moderate boiling point range and a suitable flash point, such as Kerosene, Shellsol (various grades), Escaid (various grades), Solvesso and similar products.

- 10 The diluent can be added at a concentration sufficient to make up a total of 100% for the mixture.

Extractions can be carried out in the temperature range between 10 °C and 70 °C and preferably between ambient and 45 °C.

- 15 The aqueous pregnant feed solution to be treated can also contain moderate amounts of non-complexing cations, such as nitrate, chlorate or perchlorate, and also appreciable amounts of chloride up to a concentration of 3 Molar.

- 20 Extractions can be carried out at an aqueous pH between 0.0 and 6.0, the preferred pH depending on the objective of the extraction process. This value can readily be estimated from the results given in the Examples by those skilled in the art of solvent extraction-based separations.

- 25 Stripping of the organic phase can readily be effected with a dilute aqueous sulphuric acid solution at a concentration equal to or slightly higher than the change in the metal concentration in the aqueous strip solution during the process of stripping.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of examples with reference to the accompanying drawings in which:

5 Figures 1, 2 and 3 are flow diagrams of different standard solvent extraction processes, and

Figures 4 to 11 are curves of extraction efficiency as a function of pH for different extractants, with Figures 6 to 11 relating to extractants according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

10 The invention can be applied using any standard solvent extraction apparatus, consisting of an extraction section and a single or double stripping section, with an optional washing or scrubbing section in between, and suitable to simulate standard solvent extraction flow sheets as shown in any of the flow sheets in Figures 1 to 3 respectively.

15 The flow sheets shown in Figures 1 to 3 are largely self-explanatory and are known in the art. They are therefore not described in detail hereinafter.

20 In the following examples a comparison is made of the results obtained by using organic solvent extractant mixtures according to the invention and the results obtained using other extractants. Examples 1 and 2 relate to the use of organic extraction mixtures which do not fall inside the scope of the invention while the remaining Examples illustrate results obtained using organic extraction mixtures which fall within the scope of the invention.

25 **Example 1:**

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.02 Molar DNNS in

an iso-decanol (30%) – Shellsol A mixture. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 4 indicate that DNNS is a non-selective extractant for divalent cations with optimum extraction in the pH range 1.00 to 3.0.

Example 2

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) in a mixture containing 30 % iso-decanol and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 5 indicate that, with BADI only present, only copper is extracted but from an aqueous bisulphate medium. The other metals are only partly extracted, with an obvious reversal at $\text{pH} \geq 3.50$ when sulphate ions predominate.

Example 3

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.01 Molar DNNS, in a

mixture containing 30 % iso-decanol and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 6 indicate that, with both BADI and DNNS present, the metals are extracted over a wide pH range giving various opportunities for separations or purifications. One option would be the selective rejection of Zn, Mn, Mg, Ca and Pb from the other compounds presents with a basic flow sheet as shown in Figure 1, with the option of rejecting cobalt or cadmium by appropriate scrubbing (flow sheet as per Figure 2) or selective stripping (flow sheet as per Figure 3). In the absence of iron species, nickel and copper could be extracted selectively at a lower pH, with selective stripping of nickel with a flow sheet as per Figure 3. Obviously, nickel selectivity could also be obtained by prior removal of copper, e.g. by sulphide precipitation.

Example 4

An aqueous solution of metal sulphates, obtained by bioleaching a nickel sulphide concentrate, after removal of dissolved iron, containing Ni (6.33 g/l), Cu (19.7 ppm), Co (86.3 ppm), Zn (3.3 ppm), Mg (589 ppm) and Mn (11.3 ppm) was contacted with an organic mixture containing 0.57 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.15 Molar DNNS in a mixture containing 41% iso-decanol in Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the %

extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

- 5 The same aqueous solution of metal sulphates was also contacted with an organic mixture containing 1.14 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.285 Molar DNNS in iso-decanol in the absence of Shellsol A.

- 10 The results in Figure 7a and 7b indicate that, in both instances, nickel can readily be separated from cobalt, zinc, magnesium and manganese using a flow sheet as per Figure 1 or 2. Copper can also be rejected using a flow sheet as per Figure 3.

Example 5

- 15 An aqueous solution of nickel sulphate, at 0.001 Molar, was contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and different concentrations of DNNS in a mixture of iso-decanol (30%) and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

- 25 The results in Figure 8 indicate that complete nickel extraction is already obtained at a DNNS concentration of 0.005 Molar. Extraction is very effective at DNNS concentrations between 0.010 and 0.040 Molar. With a large excess of DNNS, and up to 0.06 Molar for a 0.001 Molar metal

concentration, complete extraction is still possible but only at a higher pH.

Example 6

Aqueous solutions of nickel sulphate, at 0.001 Molar, were contacted with an organic mixture containing 0.1 Molar 2-(R₅, R₆-aminomethyl)-1-decylimidazole (R-ADI), (R₆ = H, R₅ = methyl, ethyl, butyl, pentyl, hexyl, octyl, ethylhexyl or decyl and R₅ = R₆ = ethyl), 0.010 Molar DNNS in an iso-decanol (30%) – Shellsol A mixture. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 9 indicate that very effective metal extraction can be obtained with a mono-substituted amino group, in which the substituent is an aliphatic group containing between one and six carbon atoms. With a longer chain aliphatic substituent or with a double substituted amino group, extraction is less effective, requiring a higher pH for complete extraction.

Example 7

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, containing also chloride at a concentration of 0.77 Molar, were contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.01 Molar DNNS in a mixture of iso-decanol (30%) and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide

solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 10, together with those from Example 3 (Figure 6), indicate that the extraction of zinc is strongly enhanced by the presence of chloride in the aqueous phase. The extraction of copper and cobalt is only slightly enhanced and that of nickel is not affected at all. The extractability of manganese remains low and is not much affected either.

The results show that the presence of chloride, either due to circumstances or by design, is advantageous for the selective separation of certain groups of base metals such as Cu/Zn and rejection of Ca, Mg and Mn from Ni/Co. The separation between Co and Ni is smaller but remains adequate for effective removal if the cobalt is much lower than that of nickel, which is true in most instances.

Example 8

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.08 Molar Bis(2-methyl-1-decylimidazole)amine (BMIA) and 0.01 Molar DNNS, in a mixture containing 70 % iso-decanol and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 11 indicate that, with BMIA and DNNS present, the metals are extracted over a wide pH range giving various opportunities for separations or purifications. One option would be the selective rejection of Mn and Mg (and probably Ca and Pb as well) from the other compounds present with a basic flow sheet as shown in Figure 1, with the option of rejecting nickel by appropriate scrubbing (flow sheet as per Figure 2) or selective stripping (flow sheet as per Figure 3). In the absence of iron species, cobalt could be recovered selectively from zinc and copper by selective stripping with a flow sheet as per Figure 3. Overall cobalt selectivity could also be obtained by prior removal of copper and zinc, e.g. by sulphide precipitation.

REFERENCES:

- 1- J Szymanowski, "Hydroxyoximes and Copper Hydrometallurgy", CRC Press, Boca Raton, USA, 1993
- 5 2- SC Das, PG Krishna, "Effect of Fe(III) during Copper Electrowinning at Higher Current Density", Int. J. Miner. Process., 46, 1996, pp 91.
- 3- K Tanabe, T Ohgai, T Akiyama and H Fukushima, "Characteristic Behavior of Iron-Group Metals in the Purification Process using Zinc Dust", Proceedings "Zinc & Lead '95", 22-24 May 1995, Sendai, Japan, pp303.
- 10 4- K Tozawa, T Nishimura, M Akahori, MA Malaga, "Comparison between Purification Process for Zinc Leach Solutions with Arsenic and Antimony Trioxides", Hydrometallurgy, 30, 1992, pp445-461.
- 15 5- ME Chalkley, MJ Collins, IM Masters and E Ozberk, "Deportment of elements in the Sherritt Zinc Pressure Leach Process", Proceedings "Zinc & Lead '95", 22-24 May 1995, Sendai, Japan, pp612.
- 6- CJ Krauss, "Effects of Minor Elements on the Production of Electrolytic Zinc from Zinc Sulphide Concentrates", Proceedings International Symposium on Extractive Metallurgy of Zinc, Tokyo, 1985, pp 467-481.
- 20 7- GL Bolton, VB Sefton, N Zubryckj, " Removal of Manganese and Chloride Ions from Aqueous Acidic Sulphate Solution", US Patent 4,379,037, 1983.
- 8- WR Hopkins, "SX/EW: A Mature but Expending Technology", Mining Magazine, May 1994, pp256.
- 25 9- ML Steemson, GJ Sheehan and DA Winborne, "An Integrated Bioleach/Solvent Extraction Process for Zinc Metal Production from Zinc Concentrates", PCT Patent WO 94/28184, 1994.
- 10-GM Ritcey, NL Hayward and T Salinovich, "The recovery of Nickel and Cobalt from Lateritic Ores" Patent AU 4089096A1, 1996

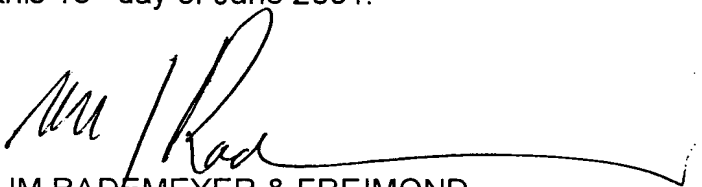
- 11-AE Norton, JJ Coetzee and SCC Barnett, "An Economically Competitive Process for the Biological Extraction of Nickel", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.
- 5 12-V Nagel, "Results from the Downstream Unit Operations of an Integrated Pilot-Plant Campaign Using the BioNIC™ Process to Produce Nickel Metal Cathode at QNI's Yabulu Refinery", Proceedings "ALTA 2000": Nickel/Cobalt – 6, Perth, Australia, May 15-18, 2000.
- 10 13-G Motteram, "Black Range Minerals Seyerston Project: A Unique Nickel Laterite", Proceedings "ALTA 2000": Nickel/Cobalt – 6, Perth, Australia, May 15-18, 2000.
- 15 14-G Motteram, M Ryan, R Berezowsky and R Raudsepp, "Murrin Murrin Nickel/Cobalt Project: Project Development Overview", Proceedings "ALTA 96": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 13-14, 1996.
- 20 15-ME Calkley, R Balán, HU Kranz and R Sánchez, "The Acid Pressure Leach Process for Nickel Cobalt Laterite: A review of Operations at Moa Nickel SA", Proceedings "ALTA 96": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 13-14, 1996.
- 25 16-A Griffin, "The Marlborough Laterites Project", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.
- 17-P Mason and M Hawker, "Ramu Nickel Process Piloting", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.
- 18-MG Baillie and GC Cock, "Weda Bay Laterite Project, Indonesia", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

- 19-KJ Hellsten and CR Lewis, "Cawse Nickel Laterite Project", Proceedings "ALTA 96": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 13-14, 1996.
- 5 20-T Kindred, "Cawse Nickel Operations Process Description and Production Ramp Up", Proceedings "ALTA 2000": Nickel/Cobalt – 6, Perth, Australia, May 15-18, 2000.
- 10 21-D Jones, J Hestrin and R Moore, "CESL Process for Nickel-Cobalt-Copper Sulphides: Testing in an integrated Pilot Plant", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.
- 22-IO Mihaylov, E Krause, SW Laundry and C van Luong, "Process for the Extraction and Separation of Nickel and/or Cobalt", Canadian Patent CA2145054AA, 1995.
- 15 23-JS Preston, "Solvent Extraction of Nickel and Cobalt by Mixtures of Carboxylic Acids and Non-chelating Oximes", Hydrometallurgy, 11, 1983, pp105.
- 20 24-JS Preston and AC du Preez, "Synergistic Effects in the Solvent Extraction of Some Divalent Metals by Mixtures of Versatic 10 Acid and Pyridinecarboxylate esters", J. Chem. Tech. Biotechnol., 61, 1994, pp159.
- 25 25-JS Preston and AC du Preez, "The Solvent Extraction of Nickel and Cobalt by Mixtures of Carboxylic Acids and Pyridinecarboxylate esters", Solvent Extr. Ion Exch., 13, 1995, pp465.
- 26-JS Preston and AC du Preez, "Separation of Nickel and Calcium by Solvent Extraction Using Mixtures of Carboxylic Acids and Alkylpyridines", Hydrometallurgy, 58, 2000, pp239.
- 27-MJ Dry, G Ioro, DF Jacobs, PM Cole, AM Feather, KC Sole, J Engelbrecht, KC Machett, PJ Cilliers, PT O'Kane and DB Dreisinger, "Cu/Co Tailings Treatment Project, Democratic Republic of Congo",

"ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy
Forum, Perth, Australia, May 25-27, 1998.

28-AM Feather, KC Sole and DB Dreisinger, "Pilot Plant Evaluation of
Manganese Removal and Cobalt Purification by Solvent Extraction",
5 Proceedings "ISEC '99": International Solvent Extraction Conference,
Barcelona, Spain, 11-16 July 1999.

DATED this 13th day of June 2001.

A handwritten signature in black ink, appearing to read 'McCallum Rademeyer & Freimond', with a long horizontal flourish extending to the right.

10 McCALLUM RADEMEYER & FREIMOND
Patent Agents for the Applicant

20014793

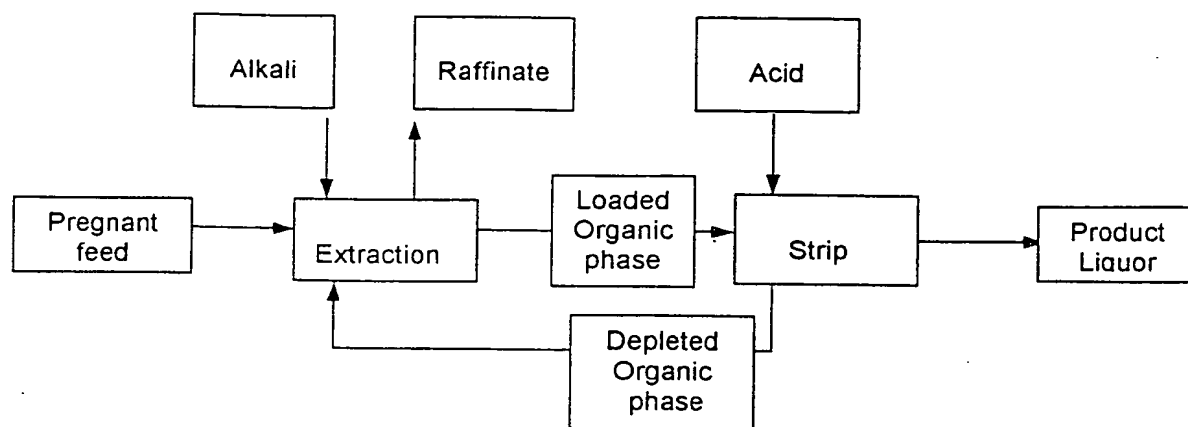


Figure 1: Basic solvent extraction flow sheet

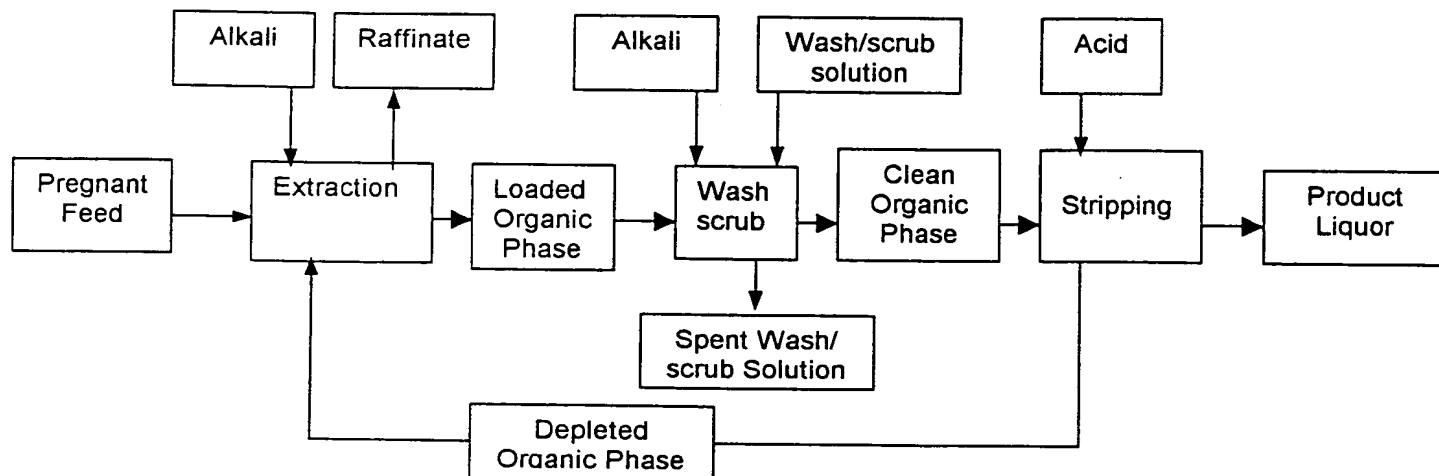


Figure 2: Solvent extraction flow sheet with wash/scrub section

McCALLUM, RADEMEYER & FREIMOND
PATENT AGENTS
FOR THE APPLICANT/s

20014793

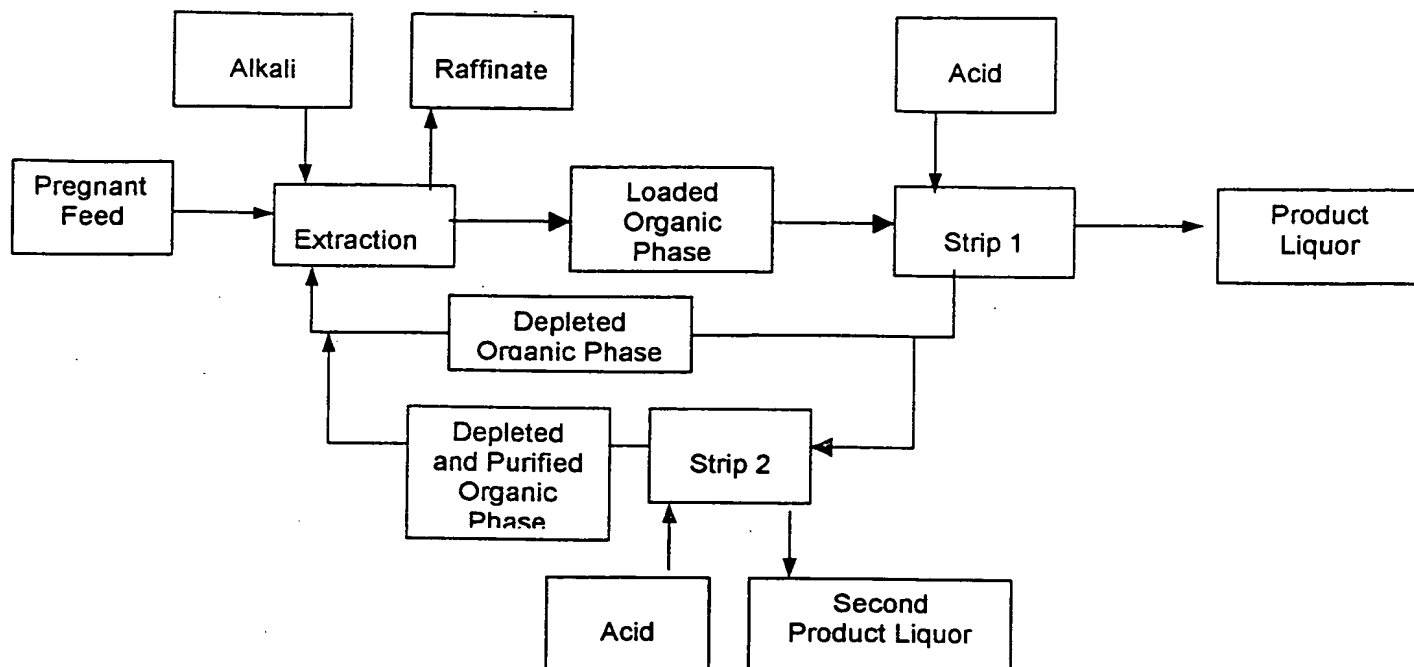


Figure 3: Solvent extraction flow sheet with second strip stage (differential stripping)

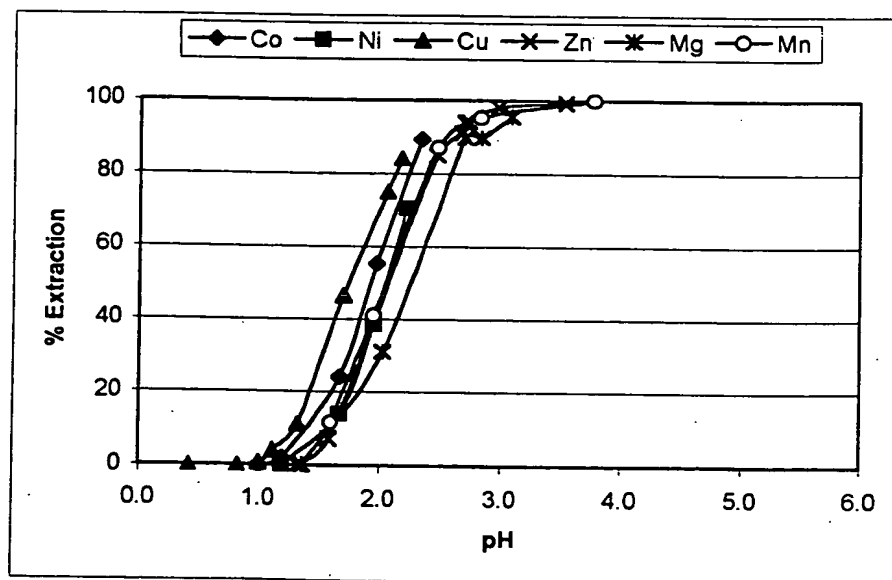


Figure 4: Extraction of individual metal ions with DNNS only

McCALLUM, RADEMEYER & FREIMOND
PATENT AGENTS
FOR THE APPLICANT/s

20014793

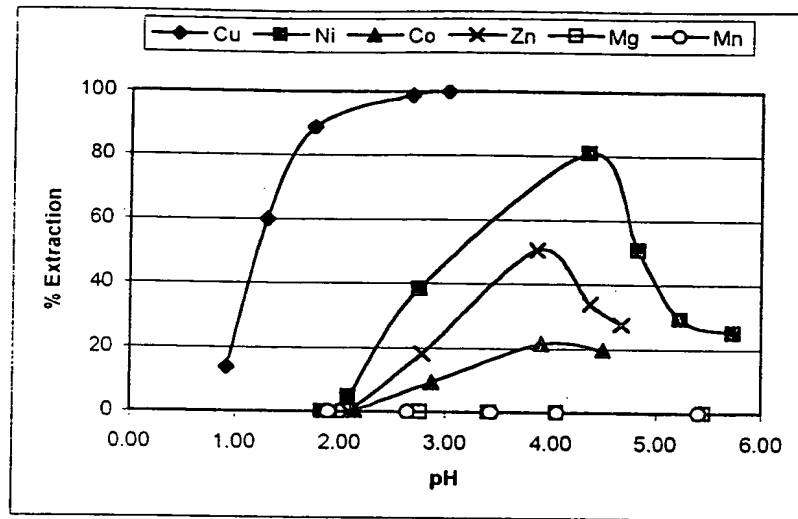


Figure 5: Extraction of individual metals with BADI in the absence of DNNS

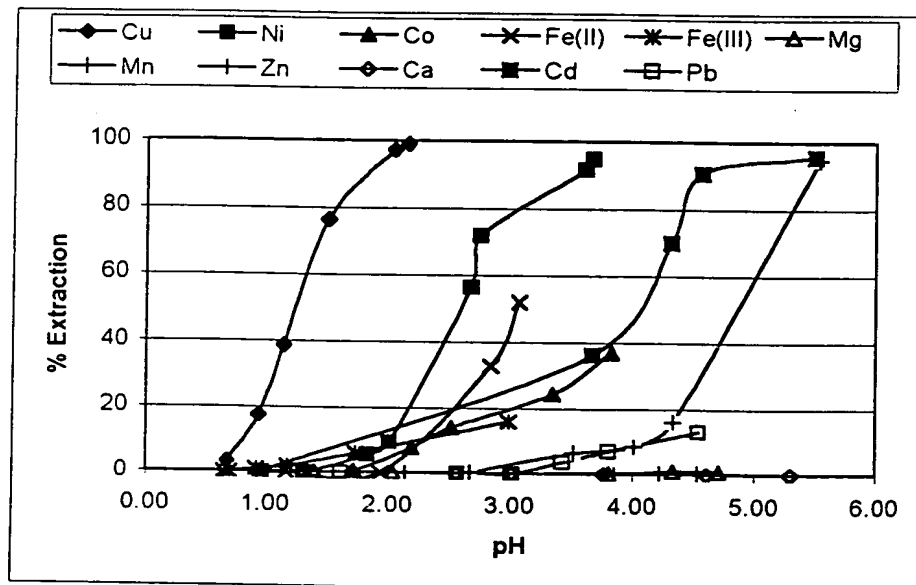


Figure 6: Extraction of individual metals with a mixture of BADI and DNNS
(low concentration)

McCALLUM, RADEMEYER & FREIMOND
PATENT AGENTS
FOR THE APPLICANT/s

20014793

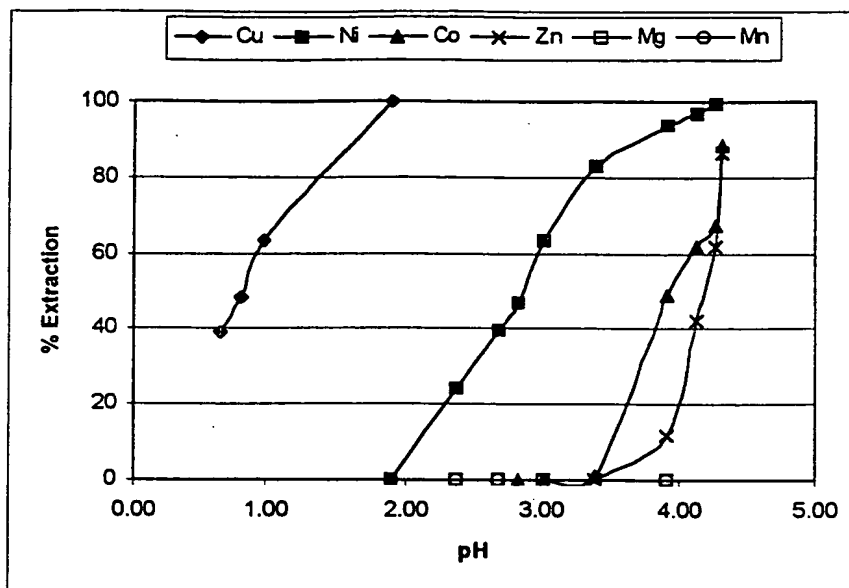


Figure 7a: Extraction of metals from a mixed aqueous solution with BADI/DNNS
(0.57 Molar BADI/ 0.14 Molar DNNS)

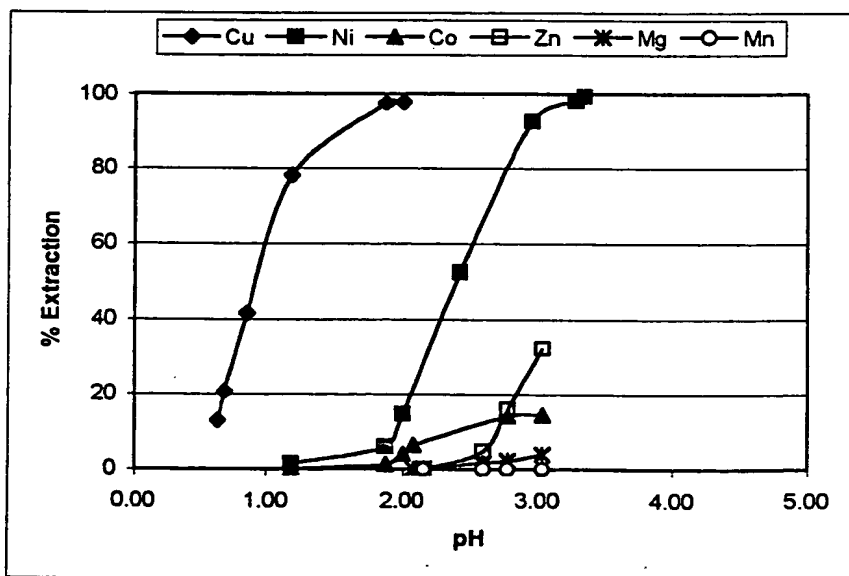


Figure 7b: Extraction of metals from a mixed aqueous solution with BADI/DNNS
(1.14 Molar BADI/ 0.28 Molar DNNS)

MCCALLUM, RADEMEYER & FREIMOND
PATENT AGENTS
FOR THE APPLICANT/S

20014793

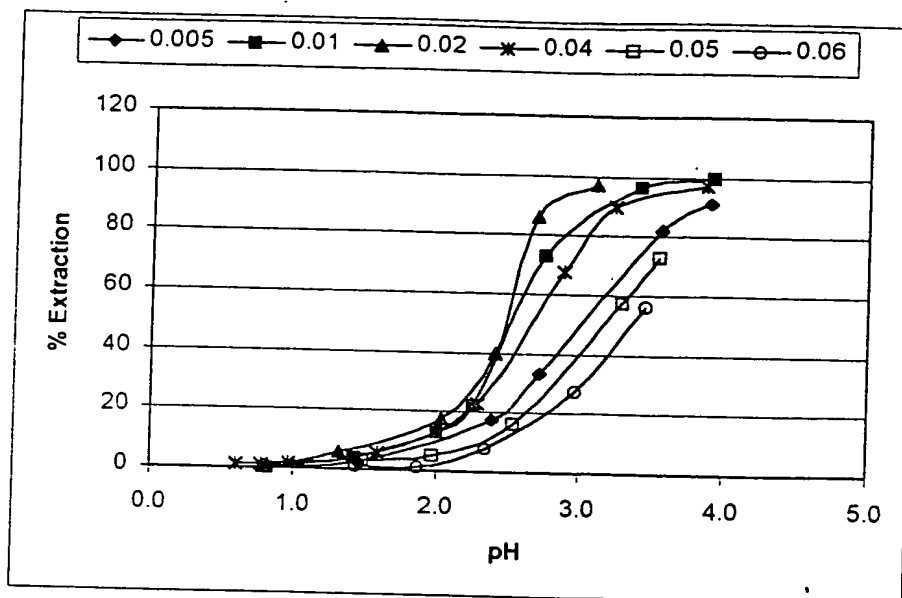


Figure 8: Extraction of nickel with a mixture of BADI and DNNS; influence of DNNS concentration (Molar)

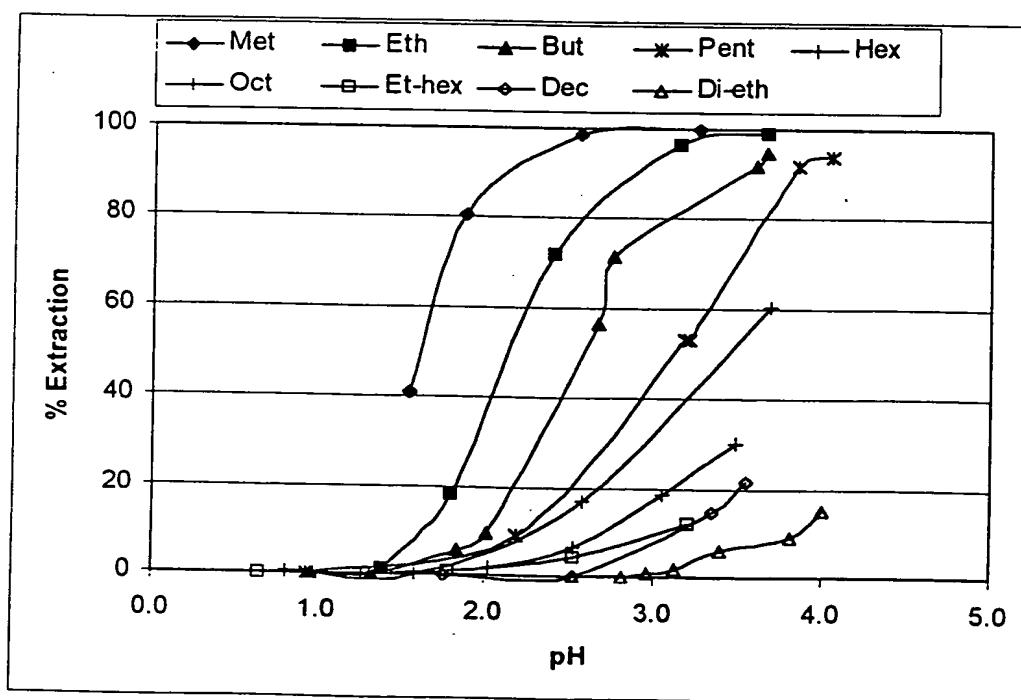


Figure 9: Effect of amino substituent in R-ADI on nickel extraction with mixtures of R-ADI and DNNS

Mar / Rad

MCCALLUM, RADEMEYER & FREIMOND
PATENT AGENTS
FOR THE APPLICANT/s